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(54) **Titanated chromium-based catalysts to produce polyethylene exhibiting better environmental stress crack resistance**

(57) The present invention relates to a supported chromium-based catalyst titanated under specific conditions and used for the homopolymerisation or the copolymerisation of ethylene. The polyethylene obtained with this catalyst has high shear resistance and environmental stress crack resistance.

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Description

The present invention relates to a catalyst for producing a high density polyethylene having a broad molecular weight distribution, in order to obtain good processability and good physical and chemical properties. The present invention further relates to a process for producing said catalyst and to the use of such a catalyst.

5 For polyethylene, and for high density polyethylene (HDPE) in particular, the molecular weight distribution (MWD) is a fundamental property which determines the properties of the polymer, and thus its applications. It is generally recognised in the art that the molecular weight distribution of a polyethylene resin can principally determine the physical, and in particular the mechanical, properties of the resin and that the provision of different molecular weight polyethylene

10 molecules can significantly affect the rheological properties of the polyethylene as a whole.

The molecular weight distribution can be completely defined by means of a curve obtained by gel permeation chromatography. Generally, the molecular weight distribution (MWD) is more simply defined by a parameter, known as the dispersion index D, which is the ratio between the average molecular weight by weight (Mw) and the average molecular weight by number (Mn). The dispersion index constitutes a measure of the width of the molecular weight distribution.

15 For most applications, the molecular dispersion index varies between 10 and 30.

Since an increase in the molecular weight normally improves the physical properties of polyethylene resins, there is a strong demand for polyethylene having high molecular weight. These high molecular weight molecules, however render the polymer more difficult to process. On the other hand, a broadening in the molecular weight distribution tends to improve the flow of the polymer when it is being processed at high shear rates. Accordingly, in applications requiring 20 a rapid transformation of the material through a die, for example in blowing and extrusion techniques, the broadening of the molecular weight distribution permits an improvement in the processing of polyethylene at high molecular weight (high molecular weight polyethylenes have a low melt index, as is known in the art). It is known that when the polyethylene has a high molecular weight and also a broad molecular weight distribution, the processing of the polyethylene is made easier as a result of the low molecular weight portion while the high molecular weight portion contributes to a 25 good impact resistance for the polyethylene resin. A polyethylene of this type may be processed using less energy with higher processing yields.

As a general rule, a polyethylene having a high density tends to have a high degree of stiffness. In general, however, the environment stress crack resistance (ESCR) of polyethylene has an inverse relationship with stiffness. In other words, as the stiffness of polyethylene is increased, the environment stress crack resistance decreases, and vice versa. 30 This inverse relationship is known in the art as the ESCR-rigidity balance. It is required, for certain applications, to achieve a compromise between the environmental stress crack resistance and the rigidity of the polyethylene.

A variety of catalyst systems are known for the manufacture of polyethylene. It is known in the art that the physical properties, in particular the mechanical properties, of a polyethylene resin can vary depending on what catalyst system was employed to make the polyethylene. This is because different catalyst systems tend to yield different molecular 35 weight distributions in the polyethylene produced. Thus for example the properties of a polyethylene resin produced using a chromium-based catalyst (i.e. a catalyst known in the art as a "Phillips catalyst") tend to be different from the properties of a product employed using a Ziegler-Natta catalyst. The production of high density polyethylene using just a chromium-based catalyst is thus desirable to enable the particular polyethylene product to be manufactured. The Encyclopedia of Polymer Science and Engineering, Volume 6, pages 431-432 and 466-470 (John Wiley & Sons, Inc., 40 1986, ISBN 0-471-80050-3) and Ullman's Encyclopedia of Industrial Chemistry, Fifth Edition, Volume A21, pages 501-502 (VCH Verlagsgesellschaft mbH, 1992, ISBN 3-527-20121-1) each discuss Phillips and Ziegler-Natta catalysts and the production of HDPE.

It is known in the art that in order to obtain the advantages of a broad molecular weight distribution, it is necessary to polymerise an intimate mixture of polyethylene molecules prepared in a common manufacturing process. It is known 45 in the art that it is not possible to prepare a polyethylene having a broad molecular weight distribution and the required properties simply by blending polyethylenes having different molecular weights.

It has thus been proposed to carry out the polymerisation by a two step process, using two reactors connected in series (GB-A-1233599; EP-A-057352; US-A-4,414,369 and 4,338,424). In a first step and in the first reactor a fraction of the high density polyethylene is produced under specified conditions and in the following second step in the second reactor a second fraction of the high density polyethylene is produced using a different set of polymerisation conditions. 50 In the two-step process, the process conditions and the catalyst can be optimised in order to provide a high efficiency and yield for each step in the overall process. The currently commercially employed two-step processes suffer from the disadvantage that because two separate serial processes are employed, the overall process has a low throughput.

It has further been proposed to produce polyethylene with a broad molecular weight distribution with a two-catalyst 55 mixture of one supported chromium catalyst and one Ziegler-Natta type catalyst (EP-A-0480376). This process suffers from the disadvantage that the Ziegler-Natta catalyst requires a co-catalyst to give an active catalytic system but the co-catalyst can influence the supported chromium catalyst and in particular can detrimentally affect its activity.

There is a need in the art for a process for producing polyethylene resins suitable for blow molding having good

environmental stress crack resistance (ESCR) which do not use a Ziegler-Natta catalyst, and in particular which use a chromium-based catalyst.

It is known in the art to provide titanium in a chromium-based catalyst. Titanium can be incorporated either into the support for the chromium catalyst or into the catalytic composition deposited on the support.

5 Titanium can be incorporated into the support by coprecipitation or terprecipitation as is the case for cogel and tergel type catalysts developed by Phillips Petroleum. Cogel and tergel catalysts respectively have binary and ternary supports. Alternatively, titanium can be incorporated into the support by impregnation of the support as described for example in US-A- 4,402,864 or by chemisorption of a titanium compound into the support as described for example in US-A-4,016,343.

10 Titanation of the catalytic composition has been disclosed in earlier patent specifications.

US-A-4,728,703 discloses that titanium can be incorporated into the catalytic composition by adding to a composite liquid suspension, of a carrier material (i.e. a support) and chromium trioxide, a titanium compound of the formula $Ti(OR)_4$.

15 US-A-4,184,979 discloses that titanium can be incorporated into the catalytic composition by adding at elevated temperature a titanium compound such as titanium tetraisopropoxide to a chromium-based catalyst which has been heated in a dry inert gas. The titanated catalyst is then activated at elevated temperature.

The ethylene polymers obtained with all the above mentioned processes do not have satisfactory mechanical properties especially with regard to the environmental stress crack resistance (ESCR).

Therefore there exists a need for a chromium-based catalyst capable of producing polyethylene resins for blow molding, having good processability and good physical and chemical properties.

20 It is an aim of the present invention to provide a catalyst for the polymerisation of ethylene to produce polyethylene having good processability.

It is another aim of this invention to provide a catalyst for producing ethylene with high environmental stress crack resistance.

25 It is a further aim of the present invention to provide a catalyst for producing polyethylene having the above described desired properties, said catalyst having a high activity.

These and other aims can be achieved with a supported titanated chromium-based catalyst prepared under specific conditions, said catalyst being used for the production of high density polyethylene with improved processability and physical and chemical properties.

30 The present invention provides a process for preparing a titanated chromium-based catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, which comprises the steps of;

- 35 a) providing a silica-containing support having a specific surface area of from 450 to 600 m^2/g ;
- b) depositing a chromium compound on the support to form a chromium-based catalyst;
- c) dehydrating the chromium-based catalyst to remove physically adsorbed water by heating the catalyst at a temperature of at least 300°C in an atmosphere of dry, inert gas;
- d) titanating the chromium-based catalyst at a temperature of at least 300°C in an atmosphere of dry, inert gas containing a titanium compound of the general formula selected from $R_nTi(OR)_m$ and $(RO)_nTi(OR')_m$ wherein R and R' are the same or different and are a hydrocarbyl group containing from 1 to 12 carbon atoms, n is 0 to 3, m is 1 to 4 and m+n equals 4, to form a titanated chromium-based catalyst having a titanium content of from 1 to 5 % by weight, based on the weight of the titanated catalyst and
- e) activating the titanated catalyst at a temperature of from 500 to 900°C.

45 The present invention further provides a catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, the catalyst comprising a silica-containing support having a specific surface area of from 450 to 600 m^2/g , a chromium compound deposited on the support, and a titanium compound comprising from 1 to 5 % by weight, based on the weight of the titanated catalyst.

50 The present invention also provides a process for producing polyethylene, in the presence of a chromium-based catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, the catalyst comprising a silica-containing support having a specific surface area of from 450 to 600 m^2/g , a chromium compound deposited on the support, and a titanium compound comprising from 1 to 5 % by weight, based on the weight of the titanated catalyst.

55 The present invention further provides the use of the catalyst of the invention in the production of high density polyethylene for providing a high environmental stress crack resistance and a low incidence of melt fracture when melted and subjected to rotational shear at varying speeds.

The present inventors have observed that the titanation, under specific conditions, of a chromium-based catalyst

having a large surface area can unexpectedly yield high density polyethylene having a very high environmental stress crack resistance (ESCR) and a low melt fracture index.

The silica-containing support material used in the catalyst of this invention can be any catalytic support known in the art. The support is an inorganic, solid, particulate porous material inert to the other components of the catalyst composition and to any other active components of the reaction system. Thus, suitable supports are inorganic materials, such as silica either alone or in combination with other metallic oxides, e.g., silica-alumina or silica-titania.

The support used in this invention has a large surface area, preferably from 475 to 550 m²/g. The support preferably has a pore volume of from 1 to 3 cm³/g, more preferably from 1.3 to 2.5 cm³/g. It is preferred that the support be dried prior to any chromium species being deposited onto it.

Known chromium-containing compounds capable of reacting with the surface hydroxyl groups of the silica-containing supports can be utilised to deposit the chromium thereon. Examples of such compounds include chromium nitrate, chromium trioxide, chromate esters such as chromium acetate, chromium acetylacetone and t-butyl chromate, silyl chromate esters and phosphorous-containing esters. Preferably, chromium trioxide is used.

A particularly preferred chromium-based catalyst may comprise from 0.5 to 3 % by weight of chromium, preferably about 1 % by weight of chromium, on a catalyst support, such as a composite silica and titania support.

The support is dried by heating or pre-drying of the support with an inert gas prior to use thereof in the catalyst synthesis, in the manner known to those skilled in the art, e.g. at about 200°C for from 8 to 16 hours.

The chromium-based catalyst can be prepared by dry mixing or non-aqueous impregnation but is preferably prepared by impregnation of silica with an aqueous solution of a soluble chromium compound such as CrO₃.

The supported chromium-based catalyst is then dehydrated preferably by heating in a stream of fluidising dry inert and non-oxidising gas, such as nitrogen, at a temperature of at least 300°C, for 0.5 to 2 hours in order to remove substantially all physically adsorbed water. The removal of physically adsorbed water avoids the formation of TiO₂ as a product from the reaction of water with the titanium compound subsequently introduced during the titanation procedure, as described below.

In a next step, the supported chromium-based catalyst is loaded with a titanium compound. The titanium compound may be of the formula R_nTi(OR')_m or (RO)_n Ti(OR')_m where R and R' are the same or different and can be any hydrocarbyl group containing 1 to 12 carbon atoms, n is 0 to 3, m is 1 to 4 and m+n equals 4. Preferably, the titanium compound is a titanium tetraalkoxide Ti(OR')₄ where R' can be an alkyl or a cycloalkyl group each having from 3 to 5 carbon atoms. The titanation is performed by progressively introducing the titanium compound into the stream of dry, inert non-oxidising gas described hereabove in the dehydration step. In the titanation step, the temperature is, as for the dehydration step, maintained at at least 300°C. Preferably, the titanium compound is pumped as a liquid into the reaction zone where it vaporises. This titanation step is controlled so that the titanium content of the resultant catalyst is from 1 to 5 % by weight, and preferably from 2 to 4 % by weight, based on the weight of the titanated chromium-based catalyst. The total amount of titanium compound introduced into the gas stream is calculated in order to obtain the required titanium content in the resultant catalyst and the progressive flow rate of the titanium is adjusted in order to provide a titanation reaction period of 0.5 to 1 hour.

After the introduction of the titanium compound has been terminated at the end of the reaction period, the catalyst is flushed under the gas stream for a period of typically 0.75 hours.

The dehydration and titanation steps are performed in the vapour phase in a fluidised bed.

The titanated catalyst is then subjected to an activation step in dry air at an elevated activation temperature for at least 6 hours. The activation temperature preferably ranges from 500 to 900°C, and is most particularly around 650°C. The atmosphere is progressively changed from nitrogen to air, and the temperature is progressively increased, from the titanation step to the activation step.

The resultant titanated chromium-based catalyst has a very high activity.

In the preferred polymerisation process of the present invention, the polymerisation or copolymerisation process is carried out in the liquid phase, the liquid comprising ethylene, and where required an alpha-olefinic comonomer comprising from 3 to 10 carbon atoms, in an inert diluent. The comonomer may be selected from 1-butene, 1-hexene, 4-methyl 1-pentene, 1-heptene and 1-octene. The inert diluent is preferably isobutane. The polymerisation process is typically carried out at a polymerisation temperature of from 85 to 110°C, preferably from 95 to 105°C and at a pressure of from 20 to 45 bars, preferably from 40 to 42 bars.

Typically, in the polymerisation process the ethylene monomer comprises from 0.5 to 8 % by weight, typically around 6 % by weight, of the total weight of the liquid phase. Typically, in the copolymerisation process the ethylene monomer comprises from 0.5 to 8 % by weight and the comonomer comprises from 0 to 4 % by weight, each based on the total weight of the liquid phase.

Whilst the operating conditions, such as the temperature and pressure of polymerization in the reactor, and the catalyst's preparation conditions, such as the surface area of the support, obviously have an influence on the properties of the polymer, titanation of the catalyst under the specific conditions described above improves the ESCR, all other factors being substantially equal.

The titanated chromium-based catalyst is introduced into the polymerisation reactor. The alkylene monomer, and comonomer if present, are fed into the polymerisation reactor. In the preferred process of the present invention, the polymerisation or copolymerisation process is carried out in a liquid-full loop reactor; after a residence time in the reactor of 0.5 to 2 hours, and preferably of about one hour, the polyethylene is recovered and transferred to one or more settling legs where the concentration in solids is increased by gravity. The solid content in a loop reactor is typically 30 to 40 % by weight; the concentration in a settling leg can be up to 60 % by weight. The polymerisation product of high density polyethylene is discharged from the settling legs and separated from the diluent which can then be recycled.

The polyethylene obtained with the catalyst of this invention has a broad molecular weight distribution (MWD) which is represented by the dispersion index D of typically from 12 to 23 and a high density typically from 0.950 to 0.960 g/cm³.

It is surprisingly observed that the polyethylene obtained with the catalyst of this invention has much higher environmental stress crack resistance (ESCR) and a much lower melt index than those obtained using the processes and catalysts of the prior art as summarised above, while keeping similar melt indices and densities. The polyethylene obtained in accordance with the invention also has a very high shear resistance (SR) defined as HLMI/MI2 where HLMI is the high load melt index measured at 190°C and under a load of 21.6 kg and MI2 is the melt index measured at 190°C under a load of 2.16 kg, both with the ASTM D-1238 standard method. The high shear resistance can result in suppression of the melt fracture phenomenon.

The following Examples are given to illustrate the invention without limiting its scope.

20 Examples 1 to 7.

A silica support was impregnated with 1 wt% chromium by the following steps. 60 g of silica were dried by heating for one hour at 130 °C, and then for 3 hours at 500 °C. The silica was allowed to cool for 45 minutes in a desiccator. 50 g of the dried silica were placed under vacuum for 30 minutes. A solution was prepared by dissolving 3.498 g of chromium acetylacetone in 250 ml of acetone. The solution was added to the dried silica drop by drop until the silica was completely saturated. Then the rest of the solution was added in a slow continuous stream. The saturated silica was agitated for 2 hours, then left overnight. The acetone was evaporated off at a temperature of 70 °C and under a pressure decreasing from 400 to 200 mbars until a fine, dry powder was obtained. The catalyst was then completely dried in an oven at 110 °C overnight.

30 This chromium-treated support was then introduced into an activator vessel incorporating a fluidised bed, flushed under nitrogen and the temperature was raised from room temperature to 300°C. The dehydration step was then carried out at this elevated temperature for 2 hours. After the dehydration step, titanium tetraisopropoxide, stored under anhydrous nitrogen, was progressively injected in the bottom of the activator vessel incorporating the fluidised bed. The amount of titanium tetraisopropoxide injected was calculated in order to give the required titanium content in the resultant catalyst and the flow thereof was adjusted in order to continue the injection to complete the desired level of titanation in around 30 minutes. After the injection was completed, the catalyst was flushed under nitrogen for around 45 minutes. Nitrogen was then progressively switched to air and the temperature was raised to the activation temperature of around 650°C for the subsequent activation step. In the activation step, the titanated chromium-based catalyst was maintained at the activation temperature for 6 hours. At the end of the activation step, the temperature was progressively decreased to 350°C. At continued cooling from 350°C to room temperature, the catalyst was flushed under nitrogen.

40 Example 8.

The polymerisation of ethylene was carried out using the same procedure as in Examples 1 to 7 but the dehydration and titanation temperatures were both 400°C.

45 Table I specifies for each of Examples 1 to 8, the nature and the specific surface area of the support, the titanium weight percent, and the dehydration, titanation and activation temperatures.

The polymerization of ethylene was carried out in one liquid-full loop reactor in accordance with the polymerization process described above and in the presence of the catalyst of each Example prepared under the conditions specified above.

50 The polymerisation conditions for each of Examples 1 to 8 are also specified in Table I. In Example 7, a cocatalyst TEAL (triethylaluminium) was employed in the polymerisation process in the amount specified in Table II.

For each of Examples 1 to 8 the pressure was 42 bars; the diluent was isobutane and the comonomer was 1-hexene.

55 The weight percent of ethylene and 1-hexene are given in Table I.

The resulting melt index MI2, shear resistance SR, density, molecular weight distribution as represented by the dispersion index D, ESCR and melt fracture are also given in Table I. The melt indices were measured with the ASTM D-1238 method at a temperature of 190°C and under a load of 2.16 kg for MI2 and 21.6 kg for HLMI. The ESCR values

referred to herein are the Bell ESCR F50 values as determined in accordance with ASTM D-1693-70, Procedure B.

All the Examples shown in Table I have a surface area of the support larger than 450 m²/g, are dehydrated and subsequently titanated at an elevated temperature and are activated at a temperature of about 650°C. All the resultant polyethylenes exhibit simultaneously the desired properties of high stress crack resistance ESCR and low incidence of melt fracture when melted and subjected to rotational shear at varying speeds. Examples 3 to 7 for which results are available at rotational speeds of 20, 40 and 60 rotations per minute showed no fracture.

Comparative Examples 1 and 2.

10 The polymerization of ethylene was carried out using the same procedure as in Examples 1 to 7 but the catalyst was not titanated.

Comparative Examples 3 to 5.

15 The polymerization of ethylene was carried out using the same procedure as in Examples 1 to 7 but the catalyst's titanation was obtained by impregnation as described in US-A-4,402,864 and triethylaluminum was used as a cocatalyst.

Comparative Examples 6 and 7.

20 The polymerization of ethylene was carried out using the same procedure as in Examples 1 to 7 but the chromium catalyst was not titanated and triethylaluminum was used as a cocatalyst. The surface area of the catalyst was only 316m²/g for each of these Comparative Examples.

25 Comparative Example 8.

The polymerization of ethylene was carried out using the same procedure as in Examples 1 to 7 but the catalyst's support had a small surface area (308 m²/g) and contained titania. The catalyst was not titanated. Triethylaluminum was used as a cocatalyst.

30 Comparative Example 9.

35 The polymerization of ethylene was carried out using the same procedure as in Examples 1 to 7 but the catalyst's support had a small surface area (280 m²/g), the chromium-based catalyst was not titanated, and triethylaluminum was used as a cocatalyst.

Comparative Examples 10 and 11

40 The polymerisation of ethylene was carried out using the same procedure as in Examples 1 to 7 but the titanated chromium-based catalyst was activated at a temperature of 750°C.

Tables II specifies for each of Comparative Examples 1 to 11, the same information as for Examples 1 to 8.

In Comparative Examples 1 and 2, the surface area is large (492 m²/g) but there is no titanation; the ESCR is high but at a rotational speed of 60 rotations per minute, melt fracture occurred in four tests in Comparative Example 1 and in three tests in Comparative Example 2. No melt fracture occurred at rotational speeds of 20 and 40 rotations per minute.

45 In Comparative Examples 3 to 5 and 8 where the titanium is in the support, the ESCR is very low.

In Comparative Examples 6, 7 and 9 where there is no titanium, the ESCR is very low.

In Comparative Examples 10 and 11, the activation temperature is 750°C; as is known in the art, that will result in poor ESCR.

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TABLE I.

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Support	Silica							
Surface area m ² /g	458	458	484	484	484	484	484	467
% Titanium by weight	2.3	2.3	4	4	4	4	4	4
Dehydration temperature (°C)	300	300	300	300	300	300	300	400
Titanation temperature (°C)	300	300	300	300	300	300	300	400
Activation temperature (°C)	650	650	650	650	650	650	650	650
Polymerisation conditions								
Temperature (°C)	106	105	104	102	102	102	102	102
TEAL (ppm)	0	0	0	0	0	0	1	0
Ethylene (wt%)	5	4.9	5.3	5.2	6	5.1	5.1	5.9
1-hexene (wt%)	0.08	0.17	0.24	0.15	0.17	0.29	0.25	0.11
Hydrogen (mole %)	0.17	0.17	0.09	0.09	0.09	0.09	0.04	0.11
Properties of polyethylene								
MI2 (g/10')	0.28	0.17	0.31	0.285	0.27	0.31	0.27	0.23
Shear response SR	84	96	86	101	96	85	97	106
Density (g/cm ³)	0.9581	0.9548	0.9544	0.9582	0.9581	0.952	0.952	0.958
Dispersion index D	13.6	14.9	13.2	13.6	13.8	15.2	15.7	14
Bell ESCR F50 (hrs)	63	179	175	76	76	169	153	61
100% Antarox								
Melt fracture	n.a.	n.a.	0	0	0	0	0	n.a.
20 rpm	n.a.	n.a.	0	0	0	0	0	n.a.
40 rpm	n.a.	n.a.	0	0	0	0	0	n.a.
60 rpm	n.a.	n.a.	0	0	0	0	0	n.a.

n.a.: not available

TABLE II.

Comparative examples	Example 1 Silica	Example 2 Silica	Example 3 Silica titan. by impregn. 490	Example 4 Silica titan. by impregn. 490	Example 5 Silica titan. by impregn. 490	Example 6 Silica	Example 7 Silica
Support							
Surface area m ² /g	492	492					
% Titanium by weight	0	0					
Dehydration temperature (°C)	-	-					
Titanation temperature (°C)	-	-					
Activation temperature (°C)	650	650					
Polymerisation conditions							
Temperature (°C)	106	106	99	99	99	108	102
TEAL (ppm)	0	0	0.8	0.8	0.8	0.8	0.8
Ethylene (wt%)	4.5	3.9	4.1	3.7	4.4	4.9	5.2
1-hexene (wt%)	0.06	0.1	0.11	0.16	0.22	0.03	0.07
Hydrogen (mole%)	0.47	0.77	0.09	0.09	0	0	0
Properties of polyethylene							
MI2 (g/10')	0.15	0.23	0.19	0.25	0.245	0.22	0.2
Shear response SR	90	82	123	114	116	82	109
Density (g/cm ³)	0.9566	0.9552	0.9558	0.9542	0.9511	0.9580	0.9587
Dispersion index D	11	9.8	13.8	13	13.2	11	9.2
Bell ESCR F50 (hrs)	84	145	31	45	58	40	<18
100% Antarox							
Melt fracture							
20 rpm	0	0	n.a.	n.a.	n.a.	n.a.	n.a.
40 rpm	0	0	n.a.	n.a.	n.a.	n.a.	n.a.
60 rpm	4	3	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. : not available

TABLE II - Continued.

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	<u>Comparative examples</u>	Example 8	Example 9	Example 10	Example 11
10	Support	Silica Titania	Silica-alum. phosphate	Silica	Silica
15	Surface area m ² /g	308	280	476	476
20	% Titanium by weight	2	0	2.4	2.4
25	Dehydration temperature (°C)	-	-	300	300
30	Titanation temperature (°C)	-	-	300	300
35	Activation temperature (°C)	650	650	750	750
40	<u>Polymerisation conditions</u>				
	Temperature (°C)	106	106	102	100
	TEAL (ppm)	0.3	0.3	0	0
	Ethylene (wt%)	4.9	4.7	3.7	5
	1-hexene (wt%)	0.09	0.1	0.09	0.2
	Hydrogen (mole%)	0	0.9	0.09	0.11
	<u>Properties of polyethylene</u>				
	MI2 (g/10')	0.32	0.15	0.31	0.31
	Shear response SR	78	126	97	96
	Density (g/cm ³)	0.9567	0.9573	0.9586	0.9558
	Dispersion index D	10.2	11.7	11.8	12

45 **Claims**

1. A process for preparing a supported chromium-based catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, which comprises the steps of;
 - 50 a) providing a silica-containing support having a specific surface area of from 450 to 600 m²/g;
 - b) depositing a chromium compound on the support to form a chromium-based catalyst;
 - c) dehydrating the chromium-based catalyst to remove physically adsorbed water by heating the catalyst at a temperature of at least 300°C in an atmosphere of dry, inert gas;
 - 55 d) titanating the chromium-based catalyst at a temperature of at least 300°C in an atmosphere of dry, inert gas containing a titanium compound of the general formula selected from R_nTi(OR')_m and (RO)_nTi(OR')_m wherein R and R' are the same or different and are a hydrocarbyl group containing from 1 to 12 carbon atoms, n is 0 to 3, m is 1 to 4 and m+n equals 4, to form a titanated chromium-based catalyst having a titanium content of from

1 to 5 % by weight, based on the weight of the titanated catalyst and
e) activating the titanated catalyst at a temperature of from 500 to 900°C.

2. A process according to claim 1 wherein the support has a specific surface area of from 475 to 550 m²/g.
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3. A process according to claim 1 or claim 2 wherein the titanium compound is a tetraalkoxide of titanium having the general formula Ti(OR')₄ wherein R' is selected from an alkyl and a cycloalkyl each having from 3 to 5 carbon atoms.
- 10 4. A process according to any one of claims 1 to 3 wherein the titanium content of the titanated catalyst is from 2 to 4 % by weight, based on the weight of the titanated catalyst.
- 15 5. A process according to any of the foregoing claims wherein the chromium compound is chromium oxide and the chromium content ranges from 0.5 to 1.5 % by weight, based on the weight of the chromium-based catalyst prior to titanation.
- 20 6. A chromium-based catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, the catalyst comprising a silica-containing support having a specific surface area of from 450 to 600 m²/g, a chromium compound deposited on the support, and a titanium compound comprising from 1 to 5 % by weight, based on the weight of the titanated catalyst.
7. A catalyst according to claim 6 wherein the support has a specific surface area of from 475 to 550 m²/g.
- 25 8. A catalyst according to claim 6 or claim 7 wherein the titanium compound comprises from 2 to 4 % by weight, based on the weight of the titanated catalyst.
9. A process for preparing polyethylene in the presence of a chromium-based catalyst for the production of high density polyethylene, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms, the catalyst comprising a silica-containing support having a specific surface area of from 30 450 to 600 m²/g, a chromium compound deposited on the support, and a titanium compound comprising from 1 to 5 % by weight, based on the weight of the titanated catalyst.
- 35 10. Use of the chromium-based catalyst produced by the process of claims 1 to 6, for producing a high density polyethylene having high environmental stress crack resistance and low melt fracture index, by polymerising ethylene, or copolymerising ethylene and an alpha-olefinic comonomer comprising 3 to 10 carbon atoms.

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DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
X	EP 0 661 299 A (PHILLIPS) * page 8, line 35 - line 59; example 32 * * page 19; example 32; table 9 * * page 20; table 10 * ---	6,7,9,10	C08F4/24 C08F10/00		
X	EP 0 647 661 A (PHILLIPS) * page 4, line 49 - line 53 * * page 6; example A1; table 1 * * page 3, line 1 - line 4 * ---	6-9			
X	EP 0 352 715 A (PHILLIPS) * page 6, line 36 - line 58 * * examples 101-103; table 1 * * table 8 * ---	6-9			
X	WO 95 33777 A (WR GRACE) * page 7, line 1 - page 9, line 20 * ---	6-9			
D,A	US 4 184 979 A (KIRCH WILLIAM) * claims 1,11 * * column 4; example 4 * ---	1,3-6,8, 9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
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A	EP 0 314 385 A (MOBIL OIL) * page 11; example 1 * * page 14; example 14 * -----	1			
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
THE HAGUE	13 October 1997	Fischer, B			
CATEGORY OF CITED DOCUMENTS					
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document					
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document					